

A Study of New Semipermeable Mem-
branes Prepared by the Electro-
lytic Method.

DSSERTATION.

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

—BY—

BENJAMIN F. CARVER,
BALTIMORE, MD.

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This investigation was suggested by Professor Morse and carried on under his personal supervision. It is with pleasure that the author takes this opportunity to thank Professor Morse for the assistance he has received from him, both in the carrying on of this investigation and in the laboratory throughout his University work. The author further wishes to express his appreciation of the instruction and advice he has received from President Remsen, Professor Jones, Professor Mathews and Doctor Frazer.

A STUDY OF NEW SEMIPERMEABLE MEMBRANES PREPARED BY THE ELECTROLYTIC METHOD.

INTRODUCTION.

Since 1901, Professor Morse has been much interested in the electrolytic preparation of semipermeable membranes for the measurement of osmotic pressure. Up to this time no improvement has been made on the method of Pfeffer for the preparation of these septa. The method used by Pfeffer is beset with many difficulties and cells prepared by it generally give unsatisfactory results, as is proven by the fact that the very numerous attempts, which have been made to repeat Pfeffer's works, have met with very little success.

Pfeffer used membranes of copper ferrocyanide, calcium phosphate and Prussian blue, but only obtained results of any value with the first of these.

The highest concentration employed by him was a six per cent. solution of cane sugar, less than one-fifth normal.

The unsatisfactory results obtained by the use of the Pfeffer cell and the difficulties encountered in its preparation by his method, led to an investigation, in this laboratory by Morse and Horn in 1901, on the preparation of semipermeable membranes by electrolysis.

WORK OF MORSE AND HORN.¹

Results were obtained during this investigation which were very promising, and it was demonstrated that an active membrane could be deposited electrolytically with much more ease than by the Pfeffer method. At first ordinary battery cells were used and membranes of copper ferrocyanide were deposited in them, which showed osmotic activity. Cups of various kinds were then tested and it was found that active membranes could be deposited in all of them without difficulty. Bottle-shaped cells, made by a local potter, were then tried with a view of testing the power of elec-

¹ Amer. Chem. Jour., 26-80.

trolytically prepared membranes to withstand pressure. After depositing the membrane in these cells, they were filled with a normal solution of cane sugar, and closed with rubber stoppers through which glass tubes had been passed. They were then placed in beakers of distilled water, which stood on the floor, and the liquid rose in the tubes to the height of 5.5 meters (the height of the room), and then overflowed in periods ranging from six to fifteen hours. When the open manometers were replaced by closed ones containing mercury, the cells failed, not, however, in consequence of a rupture of the membranes, but as a result of the weakness of the porous walls of the cells.

The next experiments they made were with small porous cups, such as are used in making standard battery cells. With these cells, pressures as high as 4.5 atmospheres were measured by closed manometers. Owing to difficulties which were encountered in securing the manometers in the cells, no higher pressures could at that time be measured. When pressures a little above 4.5 atmospheres were reached, the sugar solution oozed out between the stoppers and the manometers and the stoppers with the manometers were forced out of the apparatus.

The investigation of Morse and Horn showed, first, that membranes could be deposited electrolytically with little difficulty; second, that a more effective means must be devised to hold the manometer in place and to prevent leaking between the stopper and manometer; and third, that ordinary porous cells are not, as a rule, suitable for the deposition of membranes to be employed in the measurement of osmotic pressures, particularly high pressures.

WORK OF MORSE AND FRAZER.¹

In 1902, Morse and Frazer continued the work of Morse and Horn and obtained some very interesting results. They found that porous cells made from coarse material were unsuitable for the measurement of high osmotic pressures, that the membrane deposited in such cells,—also in others which were not hard burned—was always located in the middle of the wall, thus leaving the inner part of the wall filled with water which dilutes the solution to an uncertain extent. With hard burned cells, which are less porous, the membranes were generally found to be depos-

¹ Amer. Chem. Jour., 28-1.

ited on the inner wall, which is a condition essential to accuracy in the measurement of osmotic pressure. They also devised a satisfactory means by which the manometer could be securely held in place and leaking at the stopper and manometer prevented.

Cells made of very fine material and hard burned were obtained from the potter. Copper ferrocyanide membranes were deposited on the inner walls of these, and pressures as high as 14.5 atmospheres for half normal and 31.4 atmospheres for normal solutions of cane-sugar were measured. Although these high pressures were obtained in some cases, it was not an uncommon occurrence that the cells cracked or leaked at lower pressures, owing to the imperfect structure of the porous walls. Only about twenty per cent. of the cells, specially made for this work, withstood high pressure before developing weaknesses of one kind or another, and it became evident that cells of greater uniformity in respect to thickness, texture and strength were required for the economical prosecution of the work.

Attempts to obtain cells of the right character from the potter having failed, an investigation of the conditions under which a suitable porous wall can be produced at will was taken up and is now in progress in this laboratory.

The results of the investigation of Morse and Frazer demonstrated that the electrolytic method of depositing the copper ferrocyanide membrane far surpasses the diffusion method of Pfeffer. But up to the time when the present work was begun, only that membrane had been deposited by the new process. The ease with which this membrane was deposited and the good results obtained with it, suggested that the method could be employed with advantage in the deposition of nearly every kind of precipitate which can be formed from electrolytes in solution, in which case it would afford a ready means of investigating a great variety of substances with respect to their character as semipermeable membranes.

It was suggested that I try the applicability of the method to the deposition of a number of compounds which had been found to have or were thought likely to possess a semipermeable character.

This paper contains the results of my investigation.

The cells which were at hand when this investigation was un-

dertaken were of four varieties : First, the ordinary battery cells, with very porous walls of irregular thickness, which could be used to demonstrate but not to measure osmotic pressure. Second, a very thick-walled variety of small ones, which were very porous. Several of these were tried and gave very unsatisfactory results, owing, apparently, to the large size of the pores. Third, some few of the variety, out of which Morse and Frazer had selected the best for their use, but these were all found to be more or less defective in their structure and unsuited to the measurement of high pressures. Fourth, the bottle-shaped variety, with a capacity of about 200 cc., which had been used by Morse and Horn. From the experience of Morse and Frazer it was clear that none of these cells were suitable for the measurement of osmotic pressures, and that some other method must, for the time being, be employed to determine the activity of the membranes which it was proposed to investigate. Accordingly, it was decided to test the membranes, either by noting the rates at which the liquids rose in open manometers, or by ascertaining the rates at which the cells delivered their contents under a pressure only slightly above that of the atmosphere.

THE REMOVAL OF AIR FROM THE CELL WALLS.

The method used for the removal of air from the walls of the cell was the same, with a few unimportant modifications, as that used by Morse and Horn. The mouth of the cell, where the stopper was to come in contact with the porous wall, was covered with a thin coating of shellac in order to prevent the formation of a membrane in that place, which might easily be ruptured in removing the stopper, thus affording an opportunity for leakage when the cell was in operation.

The cell was then closed with a rubber stopper, S, Fig. 1, through which a glass tube, a, passed, the lower end of the tube being flush with the stopper. Two side tubes, b and c, were fused into the tube a, the tube b serving as an exit for the liquid as it rises in the cell, in consequence of the "endosmose," while the wire attached to the inner electrode g is passed through c. Through the tube a, the dropping funnel d was passed, the lower end of which reached nearly to the bottom of the cell. It was held in place by a piece of rubber tubing at h. The inner electrode g

consisted of a small cylinder of platinum foil, to which a piece of platinum wire had been welded ; this wire passed up between the tubes a and d and out through the side tube c. The cell, thus arranged, was placed within a large platinum cylinder, F, which

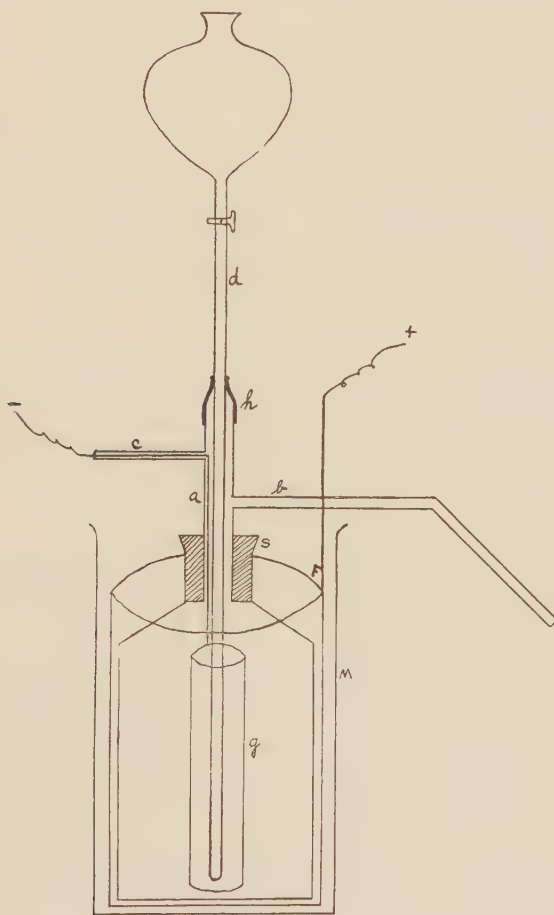


Fig. I.

completely encircled it, and served as the outer electrode. The whole was then placed in a breaker, m, and the electrodes connected with the dynamo in such a manner that the current passed from f to g. It had been shown by Morse and Horn that the air

could be completely removed from the walls of a cell by means of the strong "endosmose" which manifests itself when a porous wall is made to separate a dilute solution of a salt into two portions, and a current passed from an electrode in one of these to an electrode immersed in the other.

Hence a 0.05 per cent. solution of potassium sulphate was introduced into the cell, through the dropping funnel d, until the liquid reached the side tube b. The beaker was also filled with the solution until the cell was completely covered. "Endosmose" appeared at once, and there was a rapid flow of the liquid from without, through the wall into the cell, sweeping the air with it. The overflow which escaped through the tube b was collected and measured. Generally a current was maintained, which gave an overflow of about 500 cc. per hour.

From time to time, more of the solution was filled into the beaker to replace that which had passed through the walls of the cell. After about a liter had been forced through the walls in the manner described, the solution was partially replaced by distilled water, and the current continued until 200 cc. more of the liquid had been collected. Finally, the cell was removed, rinsed with distilled water and replaced.

The beaker and cell were filled with distilled water and the electrolysis continued. This operation was repeated until a very high resistance was obtained, showing that the liquid was practically free from the salt. The walls were now free from air and filled with nearly pure water, and the cell was ready for the deposition of the membrane. If it was not convenient to deposit the membrane immediately, the cell was filled with distilled water and placed in a beaker containing the same, where it was allowed to remain until required.

DEPOSITION OF THE MEMBRANE.

The method used to deposit the membrane was fundamentally the same as that used by Morse and Horn. The wet cell, with its walls filled with water, was fitted up in the same manner as it had been for the removal of the air, with the exception that the outer electrode, which was platinum in that case, was replaced by one of copper, zinc or nickel, etc., according to the composition of the membrane which was to be deposited. The electrodes were con-

nected with the dynamo or directly with the battery and the solutions filled in as nearly simultaneously as possible.

In the beginning, owing to the fact that the porous walls were filled with nearly pure water, there was very little current. The current, however, within a very short time began to increase. Then, within a few minutes, when the membrane started to form, it began to fall, and continued thereafter to decrease steadily until the maximum resistance of the cell for the current employed was reached. This varied greatly. Ordinarily, it was above 800 ohms and in one case exceeded 14,000, while in another it was only 300 ohms. The resistance depends to a great extent on the size of the pores of the cell, the less porous giving the higher resistance, owing, no doubt, to the better support afforded to the membrane by walls having a closer texture.

The battery, which was used in this work, consisted of fifty-five storage cells, divided into three sections, any one of which could be used separately or in combination with either or both of the others. With this arrangement a current with an electromotive force, ranging from 12 to 110 volts, was available. If a higher electromotive force was required, as was the case sometimes, the battery current was transformed by a one-horse power motor-generator to a 220-volt current. There was in series with the field of the dynamo a rheostat of so wide a range that it was possible to depress the voltage by small intervals from its maximum, *i. e.*, 220 to 20 volts.

The deposition of the membrane, in all cases, was begun with a 12-volt current, but when the resistance of this had increased to its maximum, a current with a higher electromotive force was employed, and so on until the current from the entire battery (110-volts) was in use, and, if this did not suffice, the battery current was transformed as described above. When the maximum resistance was reached with this current, the deposition was discontinued. In some cases, however, the deposition was completed with a lower voltage, owing to the fact that with a higher electromotive force, the current appeared at times to tear through the membrane causing the resistance to decrease rapidly. Whenever this occurred the voltage was depressed to that which had been in use previous to the break and the deposition completed with a current of lower electromotive force.

The formation of a membrane, that is, the time required to reach the highest resistance, usually occupied from an hour and a half to two hours.

At first there was always some "endosmose" in the direction of the current, but this always decreased as the deposition of the membrane progressed.

During the formation of the membrane it had been found necessary to replace the solution within the cell, from time to time, with a fresh one, in order to prevent the accumulation of alkali, which acts injuriously on the membranes. This difficulty was overcome very satisfactorily by filling the dropping funnel with the solution, and allowing it to run slowly into the cell during the deposition of the membrane.

As stated in the description of the apparatus, the lower end of the dropping funnel was placed near the bottom of the cell, so that the fresh liquid entered below, pushing the alkaline solution above out of the cell continuously.

Having completed the formation of the membrane, the cell was emptied, rinsed several times, within and without, with distilled water and then, if not immediately required, it was placed in distilled water, filled with the same, and allowed to stand until it was needed for use.

METHODS USED FOR DETERMINING THE ACTIVITY OF THE MEMBRANES.

As stated before, the cells employed in this investigation were not suitable for the measurement of osmotic pressure with closed manometers. Therefore, the following two methods were used to determine the activity of the membranes :

1. The cell, after the deposition of the membrane had been completed, was rinsed several times with distilled water and finally with small portions of the sugar solution (normal in all cases), which was to be used. The cell was then filled with the same, closed with a rubber stopper through which an open glass tube of small bore passed. It was then immersed in water and the height to which the liquid rose in the tube noted. As the liquid rose, other lengths of glass tubing were added until the ceiling of the room was reached.

2. The cell, after being treated as above, was closed with a stopper, through which one end of a glass tube, bent twice at right angles, was passed. The outer descending limb of the tube was cut off at a point a little above the level of the water in which the cell was immersed in order not to produce a siphon. The liquid, which was delivered at a pressure a little above that of the atmosphere, was collected in measuring cylinders, and observations taken from time to time. Thus it was possible to determine the amount of liquid delivered in any given time.

THE MEMBRANES INVESTIGATED.

The membranes deposited and examined during this investigation are, in the order in which they were tried, the phosphates of calcium and copper, the ferrocyanides of cadmium, zinc, and nickel, the sulphide of cadmium, and the cobalticyanides of cobalt, nickel, copper, and iron. The results obtained with these membranes are as follows :

1. *Calcium Phosphate.*

This compound had been employed by Pfeffer and was found to be semipermeable, but the results he obtained with it were not very satisfactory. In preparing the cells by his diffusion method, he used solutions of calcium chloride and of sodium phosphate. In this investigation tenth-normal solutions of calcium acetate and of sodium phosphate were employed. The membrane was first deposited in the walls of ordinary battery cells, the electrodes both being of platinum. When the cells, after the formation of the membrane, were partly filled with normal solutions of cane sugar, and immersed in distilled water, the level of the liquid within rose slightly, thus indicating some, but not very great, osmotic activity. When the porous cups were broken, the membrane was found to have been deposited just within the inner wall. Its appearance resembled somewhat that of wax. The phosphate was next deposited in the smaller variety of porous cups. These were filled with normal solutions of sugar, closed with rubber stoppers carrying open manometers, and placed in distilled water. The liquid rose in the tubes to heights ranging from one-half to two meters. The liquid in the tubes then became stationary for several hours and finally began to fall. As this behavior of the cell

indicated that the porous wall did not afford the membrane sufficient support, it was suggested that an attempt be made to partially close the larger pores of the wall by introducing into them some crystalline precipitate before depositing the membrane. With this object in view, cells, from which the air had been previously removed, were filled with a solution of sulphuric acid and surrounded by a solution of barium nitrate. The current was then passed for some time from the outer to the inner electrode, thus forcing the barium and sulphuric acid ions in opposite directions through the walls and filling them with barium sulphate. The cells which had received this preliminary treatment were found to be little, if any, more effective than the others. It was, therefore, evident that no advantage was to be gained by plugging the larger pores in this manner before depositing the membrane, and the attempt was abandoned. The cells, when broken, showed that the barium sulphate had been deposited in one part of the wall, while the calcium phosphate was found in another, both deposits being continuous. Although the calcium phosphate membrane is easily deposited by electrolysis, and exhibits osmotic activity, it does not appear to possess this quality in the marked degree found in some of the compounds to be mentioned hereafter.

2. *Copper Phosphate.*

Membranes of copper phosphate were deposited in cells of the same varieties as were used in examining the phosphate of calcium. Tenth-normal solutions of copper sulphate and of sodium phosphate were used in preparing the membranes. The inner electrode was of platinum, while the outer one was of copper. The membranes all showed osmotic activity, and the results obtained were, in general, about the same as those obtained with the calcium salt. The membranes, like those of calcium phosphate, were found to be located just within the inner wall of the cells. The results obtained with the calcium and copper phosphates, as well as the results obtained by others working in this laboratory with this class of salts, appear to warrant the conclusion, that the phosphates in general are not very active as semi-permeable membranes.

3. *Cadmium Ferrocyanide.*

Tenth-normal solutions of cadmium sulphate and of potassium

ferrocyanide were employed in preparing this membrane. Both electrodes were of platinum.

When a solution of cadmium sulphate is treated with the ferrocyanide of potassium, a white amorphous precipitate of cadmium ferrocyanide is formed, which is dissolved by hydrochloric acid and, likewise, by potassium hydroxide. The behavior with the latter made it necessary to prevent the accumulation of alkali in the cell during the deposition of the membrane. The arrangement by which this was accomplished has already been explained. Resistances ranging from 800 to 1500 ohms were obtained while depositing the cadmium ferrocyanide membranes in the bottle-shaped cells, which were the only ones used in this and the subsequent work.

CELL NO. I.

The first cell prepared, as described above, was set up with a normal solution of sugar. An open tube about a meter and one-half in length was passed through the stopper closing the cell. The liquid rose to the top of the tube and began to overflow in a little less than five hours and continued to overflow for several days. The cell was then taken down, refilled with a fresh sugar solution, and several lengths of glass tubing were added to the original open manometer. After the liquid had reached the height of about two meters the membrane broke.

Several other membranes of cadmium ferrocyanide were deposited and although, in every case, in the beginning the liquid was forced upwards in the manometer at the rate of about two meters per hour, in none of them did it reach a height much over two meters before the membrane gave way. When these cells were rinsed with distilled water, before filling them with sugar solution, the water became clouded with small particles of precipitate, which were detached during the rinsing of the cell. When the cells were broken, the precipitate was found to be deposited on the inner surface of the wall, and parts of the membrane could be readily detached. It is impossible to say at present whether a better membrane of cadmium ferrocyanide might not have been obtained under other conditions, that is, if the deposition had been effected with other concentrations of solutions, with a different electromotive force, or if better porous vessels had

been available. Nevertheless, in view of the fact that none of the other membranes behaved in the same manner, it appears probable that the cadmium ferrocyanide membrane is inferior to most of the others in respect to toughness and adhesiveness.

4. *Zinc Ferrocyanide.*

This precipitate had been used by Tammann¹ in his optical method for the demonstration of relative osmotic pressures of solutions. The vessels used in this work were of the bottle-shaped variety. Tenth normal solutions of zinc sulphate and of potassium ferrocyanide were employed in preparing the membranes; the electrodes were of platinum and of zinc, the former being placed in the potassium ferrocyanide solution within the cell, and the latter in the solution of zinc sulphate surrounding it. The white precipitate of zinc ferrocyanide, which is formed when the two solutions are brought together, was found to be insoluble in hydrochloric acid, but it was readily dissolved by potassium hydroxide. It was, therefore, necessary, as in the previous case, to prevent the accumulation of alkali by frequently replacing the solution within the cell by a fresh one, during the deposition of the membrane. The membrane in every case was deposited on the inner surface of the cell wall.

CELL NO. II.

In the case of this cell about two hours were required to deposit the membrane, that is, for it to reach its maximum resistance, which was 14,500 ohms. The voltage of the current at the end of the operation was 108, though in this, as in all the other depositions, a lower voltage was employed in the earlier stages.

The cell, provided with an open manometer, was set up in the usual manner with a normal solution of cane sugar. The liquid began to rise in the tube at the rate of about two meters per hour, but when it had reached a point a little above two meters, it suddenly ceased to rise and began to fall, showing that the membrane had been ruptured in some part of the cell. The same unsatisfactory behavior of the cell was experienced several times during the course of this investigation. One cell would give good results from the beginning, while another of the same variety

¹ Wied. Ann. 34. 299 (1888).

would prove to be almost a complete failure. This difference in behavior was due to difference in the texture of the porous walls. Those which were of open texture and contained visible channels in the walls were of little service, while those which had a closer texture and were wholly free from visible holes gave invariably good results. It should be stated, however, that many cells of only moderate excellence could be considerably improved by repeating the membrane-forming process after a rupture of the membrane. Usually the resistance of the repaired membrane considerably exceeded that of the original one.

CELL NO. III.

The second cell which was tried with a zinc ferrocyanide membrane gave much better results than the first, though the resistance of the membrane was much lower, reaching a maximum of only 3,750 ohms after one and one-half hours. The voltage of the final current was 96.

The cell was set up with a normal solution of sugar. In closing it with the stopper the liquid was forced up in the tube to a height of 0.2 of a meter.

The following table gives a few observations taken during the subsequent rise of the liquid in the manometer :

TABLE NO. I.

Time.	Height of liquid in manometer. Meters.
12.38 P.M.	0.2
12.52 "	1.0
2.00 "	3.4
2.38 "	4.3
2.51 "	4.7

The tube, when the ceiling was reached, was bent over and the overflow collected in a graduated tube. During the first eighteen hours, 19 cc. were delivered. The cell continued to deliver for several days, the rate of delivery steadily decreasing, as the solution within the cell became more dilute.

The results obtained with these two cells afford a striking example of a case, where the membrane, which apparently offered the lower maximum resistance to the current during its deposition, gave better results when tested in respect to its osmotic activity.

It would, however, be unsafe to conclude from this and similar observations that the activity of a membrane is independent of its resistance to the current, as measured by the volt and ammeter, because we have no idea of the relative areas of the membranes in different cells. The areas of cell wall covered by two membranes may be equal in a given instance, while the effective areas of the two may differ greatly, owing to differences in the texture of the clay walls. Again, it should be noted, that the resistance, which a given membrane exhibits, is a measure only of the difficulty with which the current tears the membrane in certain parts ; and, therefore, a membrane of low resistance, if it has a relatively large effective area, may prove very active and satisfactory, judged by the amount of water which passed through it, provided the pressure to which the membrane is subjected is not sufficient to rupture it.

CELL NO. IV.

This cell was prepared in the same manner as Nos. II and III. The deposition of the membrane required two hours. The maximum resistance obtained was 3,100 ohms with an electromotive force of 108 volts. The cell was set up in a manner different from that employed with the cells II and III. It was closed with a stopper carrying a small tube bent to two right angles, the free, outer, end of the tube being slightly higher than the top of the bottle, so that the contents of the cell might be delivered under a small but nearly constant pressure. The bottle was immersed to the neck in water at the temperature of the room, and the overflow collected in a graduated tube. The observations made are given in Table II.

The volume of the liquid in the filled cell was 180 cc. No attempt was made to maintain a uniform temperature, and the relative volumes of liquid delivered in equal intervals of time were, no doubt, considerably affected by the fluctuations of temperature, which amounted in some cases to 12°C.

Cell No. IV was taken down, rinsed with water and refilled with a fresh sugar solution. It was then placed in a bath, the temperature of which was 35°C, and the overflow was collected as before.

The observations made are given in Table III.

TABLE II.

Time.	Delivery in cc.	Time.	Delivery in cc.	Time.	Delivery in cc.
5.20 P.M.		10.	285.5	24 ²	404.0
7.35 "	10.0	11.	295.0	25.	413.0
9.00 "	14.5	12.	307.0	26.	419.0
9.30 "	16.0	13.	319.0	27.	427.0
10.30 A.M.	45.0	14.	329.0	28.	433.0
1 ¹	91.0	15.	338.0	29.	440.0
2.	128.0	16.	347.0	30.	445.0
3.	154.0	17.	354.5	31.	448.0
4.	182.0	18.	360.5	32.	451.0
5.	200.0	19.	367.0	33.	453.0
6.	222.5	20.	374.0	34.	456.0
7.	242.0	21.	381.0	35.	458.0
8.	260.0	22.	387.0	36.	460.0
9.	273.0	23.	392.0		

Total time of delivery, 1167 hours.

Total volume delivered, 460 cc.

TABLE III.

Time.	Delivery in cc.	Time.	Delivery in cc.	Time.	Delivery in cc.
2.30 P.M.	—	2.	127.0	7.	224.0
4.00 "	8.0	3.	152.0	8.	235.0
4.45 "	11.0	4.	175.0	9.	246.0
10.00 A.M.	58.0	5.	195.0	10.	255.0
1 ³ . "	100.0	6.	209.0	11.	263.0

Total time of delivery, 307 hours.

Total volume delivered, 271 cc.

The temperature of the bath, during the time of delivery, remained practically constant, not varying more than one degree.

The results given in the table show a greater regularity in the decrease of the successive volumes delivered in equal intervals of time, than those in the preceding table, where the temperature varied greatly from time to time.

Cell No. IV was refilled for the third time with a normal solution of sugar and replaced in the bath. The cylinders, in which the overflow was collected, were changed every twelve hours.

At this period an attempt was made for the first time to dis-

¹ Readings every twenty-four hours.

² Readings every forty-eight hours.

³ Readings every twenty-four hours.

cover how the volume of liquid delivered in a given interval of time is related to the mean concentration of the contents of the cell during the same time ; in other words, to ascertain how the rate at which water passes through a semipermeable membrane is affected by the concentration of the solution. It is to be presumed that, temperature and pressure remaining constant, the former is directly proportional to the latter, but there appears to be no experimental evidence bearing directly on the question.

In order to ascertain the mean concentration of the contents of the cell during the successive intervals, the amount of sugar delivered within each of them was determined by the method of Fehling. Knowing the amount of sugar present in the cell when it was set up, and the amount contained in the delivered liquid for each period, it is possible to calculate the mean concentration of the solution within the cell during any of the periods.

Taking as an example, the period during which 18.8 cc. were delivered, the mean rate per hour was 1.57 cc. and the mean number of grammes of sugar present in the cell was 44.9. During the previous period the mean number of grammes of sugar present in the cell was 50.0 and the mean rate per hour was 1.87 cc. Now if the volumes delivered during different periods are proportional to the mean concentration of the cell during those periods, then X in the following proportion should be equal to 1.57 :

$$50.0 : 49.9 :: 1 : X.$$

But X, or the calculated rate per hour, equals 1.67, and therefore greater than that obtained or the rate of delivery during these two periods was not proportional to the mean concentration of the cell during the same periods.

The observations made are given in Table IV.

The results given in the table below do not agree as well as they should, but taking into account the fact that the sugar was determined by the use of Fehling's solution, which is not a very accurate method, makes it evident that the unavoidable experimental error was quite large. The great differences in the results at the end of the table are largely owing to the fact that some of the sugar solution had leaked from the cell and consequently the calculated concentration of the contents of the cell

was greater than it was in reality, hence, the calculated mean delivery per hour was also greater than that obtained. When the cell was taken down the calculated amount of sugar which should have been present in the cell was 19.131 grammes. The amount found was only 9.072 grammes, showing a leakage of 10.059 grammes during the time of delivery. The error introduced into all the calculations by this leakage was small at first but increased with the time of delivery.

TABLE IV.

Column I in table—Number cc. delivered in twelve-hour periods.

Column II in table—Number grams of sugar in cell at beginning of each period.

Column III in table—Mean number of grams of sugar in cell during delivery.

Column IV in table—Calculated mean delivery in cc. per hour.

I.	II.	III.	IV.	V.
—	61.596	—	—	—
29.0	53.03	57.31	2.41	—
22.5	46.971	50.00	1.87	2.10
18.8	42.834	44.90	1.57	1.67
18.3	39.295	41.06	1.52	1.43
16.8	36.313	37.80	1.40	1.39
15.5	33.824	35.07	1.29	1.29
13.8	31.807	32.82	1.15	1.20
12.9	30.098	30.95	1.08	1.08
11.2	28.694	29.40	0.933	1.02
11.0	27.465	28.08	0.917	0.889
10.48	26.326	26.89	0.873	0.871
9.6	25.302	25.81	0.800	0.837
8.7	24.462	24.88	0.725	0.771
7.84	23.724	24.09	0.653	0.923
7.6	23.042	23.38	0.633	0.642
7.1	22.444	22.74	0.591	0.615
6.45	21.935	22.19	0.537	0.571
11.22 ¹	21.134	21.53	0.466	0.516
9.60	20.667	20.90	0.400	0.452
6.80	20.242	20.40	0.283	0.390

Cell No. IV had been refilled with sugar solution three times without any repair of the membrane, that is, without repeating in it the membrane-forming process, but the results obtained in the successive experiments with it show that the activity of the

¹ Readings every twenty-four hours. Capacity of cell 180 cc.

membrane was decreased very little, if any, by the large amount of water which passed through it.

The amount of liquid delivered during each of the three periods and the time required for its delivery in each case are as follows :

Time.		Volumes delivered.
Period 1.	1167 hours	460.0 cc.
" 2.	307 "	271.0 "
" 3.	348 "	276.8 "
Total,	1822 "	1007.8 "

5. *Nickel Ferrocyanide.*

Tenth-normal solutions of nickel sulphate and of potassium ferrocyanide were employed in preparing the membranes. The porous vessels employed were of the usual bottle-shaped variety hitherto described. The electrodes were of platinum and of nickel, the former being placed in the potassium ferrocyanide solution within the cell, and the latter in the nickel sulphate solution surrounding it. The greenish white precipitate of nickel ferrocyanide, which is formed when a solution of a nickel salt is treated with one of ferrocyanide of potassium, is insoluble in hydrochloric acid, but when treated with caustic potash it is decomposed with the formation of nickel hydroxide. It was necessary, therefore, to exercise the usual care to prevent the accumulation of alkali within the cell during the deposition of the membrane. The membrane in all cases was deposited on the inner surface of the cell wall.

CELL NO. V.

In preparing the first cell, two hours and fifteen minutes were occupied in depositing the membrane. The final current had an electromotive force of 62 volts and the maximum resistance offered by the membrane was 1500 ohms. The cell was filled with a normal solution of sugar, closed in the usual manner and placed in a beaker containing about a liter of water at room temperature. The method for testing the activity of the membrane was the same as that employed with cell IV.

The observations made upon the delivery of the cell are given in table V.

TABLE V.

Time.	Delivery in cc.	Time.	Delivery in cc.	Time.	Delivery in cc.
4.35 P.M.....	—	10.....	262.0	26.....	409.5
5.03 ".....	2.0	11.....	279.0	27.....	414.5
7.40 ".....	14.0	12.....	287.0	28.....	419.0
8.40 ".....	18.5	13.....	298.0	29.....	423.0
9.40 ".....	22.5	14.....	309.0	30.....	427.0
10.40 ".....	26.0	15.....	319.0	31.....	431.0
10.40 A.M.....	45.0	16.....	328.0	32 ²	440.0
1 ¹	81.0	17.....	337.0	33.....	451.0
2.....	110.0	18.....	346.0	34.....	462.0
3.....	136.0	19.....	356.0	35.....	470.0
4.....	161.0	20.....	365.0	36.....	478.0
5.....	182.0	21.....	373.0	37.....	485.0
6.....	200.0	22.....	381.0	38.....	492.0
7.....	217.0	23.....	388.0	39.....	498.0
8.....	231.0	24.....	395.0	40.....	503.0
9.....	244.0	25.....	402.0	41.....	507.0

Total time of delivery 1241 hours.

Total volume delivered 507 cc.

The volume of the liquid in the filled cell was 200 cc. It contained, therefore, 68.44 grammes of sugar. When the cell, which was still delivering at the rate of 2 cc. per day, was taken down, the liquid within was found to contain only 7.12 grammes of sugar. In other words, the normal solution which originally filled the cell had been reduced to about one-tenth that concentration in the course of the experiment.

No attempt was made to maintain a constant temperature and the volumes, delivered during successive equal intervals, do not decrease with any degree of regularity.

CELL NO. VI.

A second cell was prepared in the same manner as the first. Two hours were required to reach the maximum resistance which was only 800 ohms. The electromotive force of the current, with which the deposition was completed, was 95 volts. The bottle was filled with a normal solution of sugar and set up in the same manner as No. V, no attempt being made to maintain a constant temperature.

¹ Readings every twenty-four hours.

² Readings every forty-eight hours.

The observations made during the short time in which the cell was allowed to deliver are given in Table VI.

TABLE VI.

Time.	Delivery cc.	Time.	Delivery cc.	Time	Delivery cc.
4.15 P.M.....		1 ¹	123.5	4.....	228.0
5.15 ".....	9.5	2.....	163.5	5.....	256.0
10.00 A.M.....	70.0	3.....	200.5		

Total time of delivery, 138 hours.

Total volume delivered, 256 cc.

Having determined that the membrane was satisfactory, the cell was taken down, rinsed with water, refilled with a fresh normal solution of sugar, and then placed in the bath, the temperature of which was 35°.

The sugar contained in the delivered liquid was determined with Fehling's solution, as had been done in the case of cell No. IV, with the zinc ferrocyanide membrane.

The results obtained are given in Table VII.

TABLE VII.

Column I in table—Number of cc. delivered in twelve-hour periods.

Column II in table—Number of grams of sugar in cell at beginning of each period.

Column III in table—Mean number of grams of sugar in cell during delivery.

Column IV in table—Mean delivery in cc. per hour.

Column V in table—Calculated mean delivery in cc. per hour.

I.	II.	III.	IV.	V.
—	68.44	—	—	—
44.0	55.68	62.06	3.66	—
32.3	47.30	51.49	2.69	3.03
27.0	41.676	44.49	2.25	2.32
23.1	37.643	39.61	1.92	2.00
21.5	33.161	35.40	1.79	1.71
19.2	30.431	31.80	1.60	1.60
17.0	28.288	29.36	1.42	1.47
15.6	26.540	27.41	1.30	1.32

¹ Readings every twenty-four hours.

13.0	25.192	25.87	1.08	1.23
12.7	23.83	24.53	1.06	1.02
12.0	22.773	23.32	1.00	1.00
10.5	21.635	22.20	0.875	0.951
9.6	20.837	21.24	0.800	0.837
8.3	20.181	20.51	0.691	0.772
8.15	19.582	19.88	0.679	0.669
7.3	18.984	19.28	0.608	0.658
6.5	18.587	18.79	0.541	0.592
11.0 ¹	17.946	18.27	0.458	0.525
9.3	17.641	17.79	0.376	0.445
6.3	17.315	17.48	0.261	0.369

The results given in the table agree to about the same extent as those in Table IV. The same errors which entered into the calculation in that case were present also in this. The calculated amount of sugar which should have been present in the cell, when it was taken down, was 16.545 grammes, while the amount found was only 7.49, showing a leakage of 8.605 grammes during the time of the experiment.

Cell No. VI was refilled for the third time with a normal solution of sugar, closed with a stopper carrying a tube differing from those previously used in that the end of it reached nearly to the bottom of the cell. This method of procedure was followed in order to ascertain whether there was complete diffusion of the water as it entered the cell. There was reason for suspecting that the diffusion was incomplete (see Table XV); that a part of the water entering the cell through the membrane glided up the wall instead of diffusing uniformly, with the result that the liquid delivered was, in general, less concentrated than the contents of the cell. With this arrangement, if the diffusion was complete, the concentration of the delivered solution should be equal to the mean concentration of the cell during the time of delivery, but, on the other hand, if the water as it entered the cell rose to the top, as was suspected, then the concentration of the delivered liquid should be greater than the mean concentration of the cell during the period of delivery, the pressure and temperature being constant.

The cell was placed in the bath and observations made every twelve hours.

¹ Readings every twenty-four hours. Capacity of cell 200 cc.

The concentration of the delivered liquid was calculated from its specific gravity, which was determined by a Mohr-Westphal balance.

Only the first few observations made are given in Table VIII, because the sugar solution was found to have leaked through the membrane to such an extent as to render the latter observations worthless.

TABLE VIII.

Capacity of cell 200 cc.

Column I in table—Number of cc. delivered in twelve-hour periods.

Column II in table—Number of grams sugar in cell at beginning of each period.

Column III in table—Mean number of grams of sugar in cell during period.

Column IV in table—Number of grams sugar in 1 cc. of delivered solution.

Column V in table—Mean number of grams sugar 1 cc. in cell during delivery.

Column VI in table—Percentage relation of column IV and V.

I.	II.	III.	IV.	V.	VI. Per cent.
—	68.440	—	—	—	—
44.7	54.297	61.368	0.3164	0.3068	103.1
25.5	47.683	50.990	0.2594	0.2549	101.8
21.0	43.011	45.347	0.2225	0.2217	100.3
19.48	39.078	41.044	0.2019	0.2052	98.3
17.45	35.950	37.514	0.1793	0.1875	95.0

The amount of sugar found in the cell, when it was taken down, was 7.794 grammes while the calculated amount which should have been present was 22.04 grammes, showing a leakage of 14.246 grammes. The amount found in the water in which the cell had been immersed was 14.986.

Since the error, which was introduced into the calculations in consequence of the leakage of the sugar solution through the membrane, tends to lower the percentage relation between the concentration of the delivered liquid and that calculated for the contents of the cell, it is safe to conclude that, even in the case of the last two observations, the concentration of the delivered liquid was in reality greater than the mean concentration of the contents of the cell during the time of delivery, in other words, that the water as it enters the cell does not diffuse rapidly enough

to give to the delivered solution a concentration equal to that of the contents of the cell.

The present cell had been set up three times, without repairing the membrane. The amount of liquid delivered and the time occupied in delivering it are as follows :

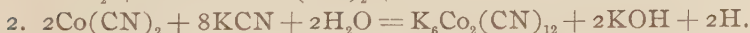
	Time.	Volume delivered.
Period 1.	138 hours	256.0 cc.
" 2.	348 "	333.4 "
" 3.	252 "	263.3 "
Total,	738 "	852.7 "

PREPARATION OF POTASSIUM COBALTICYANIDE.

Having obtained very satisfactory results with the ferrocyanide membranes it was decided to investigate some of the cobalticyanides. Since cobalticyanide of potassium is not a common laboratory reagent, it was necessary to prepare it for the intended work. As text-books give rather meager directions for its preparation, it is not out of place to mention here a few precautions, which were found necessary in order to obtain satisfactory results.

The salt was made by treating a solution of a cobalt salt (chloride or nitrate, were both used in this investigation), with a solution of potassium cyanide until all the precipitate, which was formed in the beginning, was redissolved. The precipitate formed on adding the potassium cyanide solution is the protocyanide of cobalt, and this redissolves in the excess of potassium cyanide, forming the potassium cobalticyanide.

The reactions which take place are :



The solution thus obtained was clear and had a yellowish brown color which became reddish brown on heating. The potassium cobalticyanide salt can be separated from its solution by one or two methods: First, by evaporation, when the salt separates out in well formed crystals with a slightly yellowish color; or second, by adding to the solution an excess of alcohol in which the salt is insoluble. By the second method the salt is obtained as an almost white powder. Both methods were used. The salt obtained by the first was found to contain potassium cyanide and

a solution of it gave a strong alkaline reaction. When a solution of cobalt sulphate was treated with it, a dirty pink precipitate was formed, which was dissolved by an excess of the reagent. Even after recrystallizing several times the cobaltcyanide prepared by the first method, the product gave with cobalt sulphate a brownish precipitate, but it was found that by adding acetic acid to the reagent until it became slightly acid to litmus paper, this difficulty disappeared and a clean precipitate of a rose-pink color was obtained.

This was found to be a very satisfactory means for testing the potassium cobaltcyanide solutions for alkali or potassium cyanide, before using them for the deposition of the membranes, since the presence of a very little alkali or cyanide can be detected by noting the color of the precipitate formed, when the reagent is added to a solution of cobalt sulphate. It is probable that the salt can be sufficiently freed from potassium hydroxide and cyanide by repeated recrystallizations, but the desired result is much more easily obtained by acidifying with acetic acid. Furthermore, since alkali is produced within the cell during the deposition of the membrane, it was found to be advantageous to add some acetic acid to the cobaltcyanide solution, and this was done in all cases, whether the reagent had been prepared by the first or by the second method. The best results, however, were obtained by using cobaltcyanide of potassium prepared by the first method, *i. e.*, by recrystallizing the salt twice from water and acidifying with acetic acid before using it for the deposition of the membranes.

6. Cobalt Cobaltcyanide.

Tenth-normal solutions of cobalt sulphate and of potassium cobaltcyanide were employed in preparing the membrane. The electrodes were both of platinum, the negative within the cell and the positive without.

When a solution of cobalt salt is treated with one of potassium cobaltcyanide, a rather gelatinous, rose-pink colored precipitate of cobalt cobaltcyanide is formed, which is insoluble in acids, hot and cold, but is readily decomposed by caustic potash with formation of the hydroxide of cobalt. This conduct with a caus-

tic alkali made it necessary to have acetic acid within the cell during the formation of the membrane.

CELL NO. VII.

Two hours were required for the deposition of the membrane, *i. e.*, to obtain the maximum resistance, which was only 300 ohms. The electromotive force of the current at the close was 107 volts. The membrane was found deposited on the surface of the inner wall of the cell.

The bottle was filled with a normal solution of sugar and closed in the usual manner. It was then immersed in water at the room temperature and the overflow collected in graduated tubes.

The observations made are given in Table IX.

TABLE IX.

Time.	Delivery in cc.	Time.	Delivery in cc.	Time.	Delivery in cc.
3.30 P.M.	—	11.	179.0	23.	221.0
10.00 A.M.	31.0	12.	184.0	24.	223.0
1 ¹ .	53.5	13.	189.0	25.	225.0
2.	74.5	14.	194.0	26.	227.0
3.	92.0	15.	198.0	27.	229.0
4.	109.0	16.	201.0	28.	231.0
5.	124.5	17.	204.0	29.	232.5
6.	139.5	18.	208.0	30.	234.0
7.	150.0	19.	211.0	31.	235.0
8.	160.0	20.	213.5	32 ² .	239.0
9.	169.0	21.	216.0	33.	242.0
10.	174.0	22.	218.0	34.	245.0

Total time of delivery, 781 hours.

Total volume delivered, 245 cc.

The results obtained show that the salt under investigation possesses a decided semipermeable character, however, the degree of activity in the one case tried was not as great as that observed is some of the other cobaltcyanides which were examined.

7. *Nickel Cobaltcyanide.*

Tenth-normal solutions of nickel sulphate and of potassium cobaltcyanide were employed in preparing the membranes. The inner or negative electrode was of platinum, and the outer or positive one of nickel.

When a solution of a nickel salt is treated with one of potas-

¹ Readings every twenty-four hours.

² Readings every forty-eight hours.

sium cobalticyanide, a voluminous, bluish green precipitate of nickel cobalticyanide is formed. This precipitate was found to be insoluble in acids, hot and cold, but when treated with caustic potash it was decomposed with formation of the pale green of hydroxide of nickel. Hence the usual precautions were taken in order to prevent the accumulation of alkali in the cell during the deposition of the membrane.

CELL NO. VIII.

It required two hours and forty minutes to deposit the first membrane, and then the maximum resistance obtained was only 180 ohms. The final current had an electromotive force of 96 volts.

The cell was filled with a normal solution of sugar and set up in the usual manner at room temperature.

The observations made are given in Table X.

TABLE X.

Time.	Delivery in cc.	Time.	Delivery in cc.	Time.	Delivery in cc.
2.25 P.M.	—	14.....	315.0	30.....	478.0
7.40 "	11.0	15.....	327.0	31.....	486.0
10.00 A.M.	45.0	16.....	335.0	32.....	494.0
1 ¹	85.0	17.....	343.0	33.....	503.5
2.....	110.5	18.....	352.0	34.....	512.5
3.....	136.5	19.....	360.0	35.....	519.5
4.....	161.0	20.....	368.0	36.....	523.5
5.....	183.0	21.....	375.5	37.....	527.0
6.....	202.5	22.....	383.0	38.....	530.5
7.....	222.0	23 ²	395.0	39.....	534.0
8.....	233.0	24.....	409.0	40.....	537.5
9.....	251.0	25.....	422.0	41 ³	544.5
10.....	267.0	26.....	435.0	42.....	555.0
11.....	280.5	27.....	447.0	43.....	564.5
12.....	292.5	28.....	458.0	44.....	571.9
13.....	303.0	29.....	469.0	45.....	577.5
				46.....	583.5

Total time of delivery, 1988 hours.

Total volume delivered, 583.5 cc.

The capacity of cell VIII was 210 cc. It contained in the beginning, therefore, 71.86 grams of sugar. When the cell which,

¹ Readings every twenty-four hours.

² Readings every forty-eight hours.

³ Readings every ninety-six hours.

was still delivering as the rate of 1.5 cc. per day, was taken down, the liquid within was found to contain only 3.52 grams of sugar, that is, the normal solution which originally filled the cell had become diluted to about one-twentieth of its original concentration.

CELL NO. IX.

Cell No. IX was prepared in the same manner as No. VIII. It required two hours to deposit the membrane. The maximum resistance, which was 470 ohms, was obtained with a current having a voltage of 94. It was set up in the same manner as No. VIII, but was only allowed to deliver for a few days, when it was taken down, refilled with a fresh sugar solution, and placed in the bath.

The observations made before removing it to the bath are given in Table XI.

TABLE XI.

Time.	Delivery in cc.	Time.	Delivery in cc.	Time.	Delivery in cc.
1.00 P.M.	—	1 ¹	70.0	4.....	409.5
2.00 "	7.5	2.....	92.0	5.....	143.5
10.00 A.M.	46.5	3.....	110.0	6.....	158.0

Total time of delivery, 165.0 hours.

Total volume delivered, 158.0 cc.

Having determined that the membrane was satisfactory, the cell was, as stated above, refilled with a normal solution of sugar and placed in the bath which had a temperature of 35°. The sugar in the delivered liquid was determined by the method of Fehling as had been done with cells Nos. IV and VI.

Observations were made every twelve hours, and are given in Table XII.

The results given in the table agree to about the same extent as those in Tables IV and VII.

When the cell was taken down, the calculated amount of sugar which should have been present in the cell was 23.599 grams, while the amount actually found was only 9.985, showing a leakage of 13.612 grams. Hence the calculations were vitiated by the same errors in this case as in the case of cells Nos. IV and VI.

¹ Readings every 24 hours.

TABLE XII.

Column I in table—Number of cc. delivered in twelve-hour periods.

Column II in table—Number of grams of sugar in cell at beginning of each period.

Column III in table—Mean number of grams of sugar in cell during delivery.

Column IV in table—Mean delivery in cc. per hour.

Column V in table—Calculated mean delivery in cc. per hour.

I.	II.	III.	IV.	V.
—	63.99	—	—	—
24.7	56.42	60.7	2.05	—
18.2	51.517	53.97	1.51	1.81
15.6	47.633	49.58	1.30	1.38
14.2	44.518	46.08	1.18	1.20
13.5	41.740	43.13	1.12	1.10
12.8	39.340	40.53	1.06	1.05
11.5	37.421	38.38	0.958	1.003
11.2	35.701	36.56	0.933	0.912
9.3	34.469	35.09	0.775	0.895
9.5	33.270	33.84	0.791	0.747
11.1	31.919	32.59	0.925	0.761
10.3	30.665	31.29	0.858	0.888
8.9	29.674	30.11	0.741	0.825
8.0	28.830	29.25	0.666	0.719
7.75	28.112	28.47	0.645	0.648
13.9 ¹	26.831	27.47	0.579	0.552
11.6	25.943	26.39	0.483	0.556
9.75	25.412	25.68	0.406	0.470
7.4	24.901	25.16	0.308	0.398
9.6	44.323	24.61	0.400	0.301

8. *Copper Cobalticyanide.*

Tenth-normal solutions of copper sulphate and of potassium cobalticyanide were employed in preparing the membranes. The inner or negative electrode was of platinum and the outer or positive one of copper. A turquoise-blue colored precipitate of copper cobalticyanide is formed, when a solution of a copper salt is treated with one of potassium cobalticyanide. This precipitate is insoluble in acids, hot and cold, but when treated with caustic potash, it turns green, and then becomes darker and darker in color until finally it has the black appearance characteristic of cupric oxide.

¹ Readings every twenty-four hours. Capacity of cell 187 cc.

In order to prevent the formation of cupric oxide while depositing the membrane, the solution of potassium cobalticyanide within the cell was acidified with acetic acid.

CELL NO. X.

In depositing the first membrane a maximum resistance of only 230 ohms was obtained at the end of two hours. The current, with which the deposition of the membrane was completed, had an electromotive force of 107 volts. The bottle was filled with a normal solution of sugar and set up in the usual manner at room temperature.

The observations made, in respect to the overflow, are given in Table XIII.

TABLE XIII.

Time.	Delivery in cc.	Time.	Delivery in cc.	Time.	Delivery. in cc.
12.45 P.M.	—	8.....	279.0	18.....	398.0
2.45 "	9.0	9.....	295.0	19.....	407.0
10.00 A.M.	73.0	10.....	309.0	20.....	416.0
1 ¹	113.0	11.....	324.5	21 ²	432.0
2.....	147.0	12.....	338.5	22.....	445.0
3.....	174.0	13.....	349.0	23.....	459.0
4.....	206.0	14.....	359.0	24.....	470.0
5.....	231.5	15.....	369.0	25.....	481.0
6.....	246.5	16.....	378.5	26.....	492.0
7.....	261.0	17.....	388.0	27.....	503.0
				28.....	513.0

Total time of delivery, 885 hours.

Total volume delivered, 513 cc.

Cell No. X had a capacity of 217 cc. It, therefore, contained 74.25 grams of sugar when set up. When the cell, which was still delivering at the rate of 5 cc. per day, was taken down only 8.04 grams of sugar were found in its contents. In other words, the normal solution of sugar, which originally filled the cell, had been diluted to about one-ninth the original concentration.

Cell No. X was taken down, rinsed with water, refilled with a fresh sugar solution and placed in the bath, the temperature of which was 35°.

The sugar present in the delivered liquid was determined by the

¹ Readings every twenty-four hours.

² Readings every forty-eight hours.

method of Fehling, as had been done in the case of cells Nos. IV, VI, and IX.

The observations, which were made every twelve hours, are given in Table XIV.

TABLE XIV.¹

Column I in table—Number of cc. delivered in twelve-hour periods.

Column II in table—Number of grams sugar in cell at beginning of each period.

Column III in table—Mean number of grams of sugar in cell during delivery.

Column IV in table—Mean delivery in cc. per hour.

Column V in table—Mean delivery in cc. per hour.

Column VI in table—Calculated mean delivery in cc. per hour.

I.	II.	III.	IV.	V.	VI.
—	74.257	—	35.8°	—	—
36.35	63.865	69.06	35.4°	3.03	—
27.65	56.408	60.14	35.2°	2.30	2.63
24.60	50.861	53.63	35.8°	2.05	2.05
22.50	46.327	48.59	35.4°	1.88	1.85
20.75	42.537	44.43	35.4°	1.73	1.72
19.43	39.423	40.98	35.8°	1.54	1.59
18.32	36.659	38.04	36.0°	1.53	1.38
17.40	34.516	35.59	35.8°	1.45	1.43
15.35	32.975	33.78	27.0°	1.28	1.37
13.40	31.343	32.16	22.0°	1.12	1.22
10.45	30.130	30.64	24.0°	0.87	1.06
14.13	28.610	29.37	35.0°	1.18	0.833
11.30	27.431	28.02	32.0°	0.941	1.130
12.55	26.198	26.81	36.0°	1.045	0.898
10.60	25.182	25.69	32.0°	0.883	1.03
11.12	24.147	24.66	34.0°	0.926	0.844
9.50	23.330	23.74	29.0°	0.791	0.891

During the latter half of the period in which the cell was in operation, the temperature of the bath fell several times to that of the room in consequence of accidents to the gas supply during the night. This will account for the great irregularities of temperature given in the table. The temperatures given are those of the bath, when the measuring tubes were changed. The results obtained are of little value, except as they indicate the activity of the membrane and in a rough way the effect of temperature on the amount of liquid delivered.

The amount of sugar which, according to calculations, should

¹ Capacity of cell, 217 cc.

have been in the cell, when it was taken down, was 23.33 grams, while the amount found was 19.53, showing a leakage of 3.8 grams during the experiment.

Cell No. X was refilled for the third time with a fresh sugar solution and replaced in the bath. The sugar contained in the delivered liquid was calculated from the specific gravity of the latter which was determined with a Mohr-Westphal balance. The object was to ascertain what relation existed between the concentration of the overflow and the mean concentration of the contents of the cell during the period in which the liquid was delivered. If there was complete diffusion, of the entering water, within the cell, then the two concentrations should be equal, pressure and temperature being constant. Only a few of the earlier observations are given in Table XV, however, because the error introduced into the calculations in consequence of leakage of the sugar solution through the membrane, became so large during the latter part of the experiment that the results obtained were of uncertain value.

TABLE XV.¹

Column I in table—Number of cc. delivered in twelve-hour periods.

Column II in table—Number of grams of sugar in cell at beginning of each period.

Column III in table—Mean number of grams of sugar in cell during period of delivery.

Column IV in table—Number grams of sugar in 1 cc. of delivered solution.

Column V in table—Mean number of grams of sugar in 1 cc. in cell during delivery.

Column VI in table—Percentage relations of columns IV and V.

I.	II.	III.	IV.	V.	VI. Per cent.
—	74.257	—	—	—	—
36.1	63.991	69.124	0.2844	0.3185	89.2
27.82	57.310	60.650	0.24015	0.2794	85.9
23.75	52.154	54.732	0.21711	0.2522	86.0
22.73	47.636	49.895	0.1988	0.2299	86.4
20.92	43.773	45.704	0.1799	0.2106	85.4
19.42	40.501	42.137	0.1685	0.1941	86.8
16.38	37.934	38.717	0.1576	0.1784	87.7
17.02	35.486	36.710	0.1436	0.1691	84.3

¹ Capacity of cell 217 cc.

The results make it appear that the concentration of the delivered liquid was always considerably less than that of the contents of the cell during the time of delivery and the difference is too great to be accounted for by any errors in the calculations due to leakage. It appears, therefore, that the water as it enters is not immediately diffused through the contents of the cell. The same conclusions was reached in the case of cell No. VI.

When the cell was taken down, the calculated amount of sugar within was 20.66 grams, but the amount found in the contents of the cell was only 15.47, showing that a leakage of 5.19 grams had taken place during the experiment.

Cell No. X had been filled three times with fresh sugar solution. The volumes delivered and time required for their delivery are as follows :

Time.		Volumes delivered.
Period	1. 885 hours.	513.00 cc.
"	2. 204 "	295.40 "
"	3. 252 "	331.81 "
Total, 1341 hours.		1140.21 cc.

These results show that the effectiveness of the membrane in this cell was decreased very little, if any, by the large quantity of water which passed through it.

CELL NO. XI.

Cell No. XI was prepared in the same manner as cell No. X. Two hours were occupied in reaching the maximum resistance, which was 2,750 ohms. The deposition of the membrane was completed with a current, having a voltage of 110. The cell, when set up in the usual manner, started to overflow so slowly that it was immediately taken down and the membrane-forming process repeated for a period of forty-five minutes. At the end of this time a maximum resistance of 5,550 ohms was obtained with a current having a voltage of 112.

The cell was refilled with normal sugar solution and again set up at room temperature.

The observations made are given in Table XVI.

TABLE XVI.

Time.	Delivery in cc.	Time.	Delivery in cc.	Time.	Delivery in cc.
12.55 P.M.....	—	3.....	109.0	9.....	175.0
1.55 ".....	6.0	4.....	123.0	10.....	181.0
10.30 A.M.....	44.0	5.....	136.0	11.....	186.0
1 ¹	70.0	6.....	147.0	12.....	191.0
2.....	91.0	7.....	163.0	13.....	196.0
		8.....	169.0	14.....	201.0

Total time of delivery 351.0 hours.

Total volume delivered 201.0 cc.

9. Ferrous Cobalticyanide.

Tenth-normal solutions of ferrous sulphate and of potassium cobalticyanide were employed in preparing the membrane. The electrodes were both of platinum, the negative within the cell and the positive without.

When a solution of ferrous sulphate is treated with one of potassium cobalticyanide, a slightly yellow, amorphous precipitate of ferrous cobalticyanide is formed. This precipitate is somewhat affected by strong acids, especially nitric, but acetic acid did not appear to change it. When treated with potassium hydroxide, a mixture of ferrous and ferric hydroxides was formed. It was necessary, therefore, to prevent an accumulation of alkali in the cell during the deposition of the membrane.

CELL NO. XII.

The membrane was deposited in the usual manner. Two hours and forty minutes were occupied in obtaining the maximum resistance, which was only 600 ohms. The voltage of the current, with which the deposition was completed, was 107. The cell was filled with a normal solution of sugar and closed in the usual manner. It was placed in a beaker containing about one liter of water at the room temperature. The overflow from the cell was collected in graduated tubes.

The observations made are given in Table XVII.

¹ Readings every twenty-four hours.

TABLE XVII.

Time.	Delivery in cc.	Time.	Delivery in cc.	Time.	Delivery in cc.
4.10 P.M.	—	10.	164.0	21.	257.0
10.00 A.M.	19.0	11.	173.5	22.	266.0
1 ¹	39.0	12.	181.5	23.	275.0
2.	62.0	13.	191.0	24.	284.0
3.	78.0	14.	199.0	25.	290.0
4.	92.5	15.	206.5	26.	297.0
5.	101.5	16.	214.0	27.	303.0
6.	114.0	17.	220.5	28.	308.0
7.	124.0	18.	227.0	29.	313.0
8.	141.1	19.	234.0	30.	318.0
9.	153.0	20 ²	244.0	31.	323.0

Total time of delivery, 1050 hours.

Total volume delivered, 323 cc.

The results show that this membrane possesses a decided semi-permeable character, but the activity was not as marked as that in the cases of some other membranes, especially 7 and 8. However, since the membrane was only tested in the one cell a definite opinion in respect to its activity cannot be given.

10. Cadmium Sulphide.

An attempt was made to ascertain whether cadmium sulphide possesses a semipermeable character. The results were altogether negative.

Tenth-normal solutions of cadmium sulphate and of potassium sulphide were employed in depositing the compound. The electrodes were both of platinum. In preparing the first cell of this kind, the sulphide solution was placed within the cell and the sulphate solution without. The inner electrode was negative and the outer one positive (the usual arrangement). The sulphide, however, was deposited on the outer wall, and the cell, when set up in the usual manner, failed to show the slightest activity.

A second cell was prepared with the arrangement of the solutions reversed, *i. e.*, the solution of potassium sulphide was placed without and that of the cadmium sulphate within the cell, and the direction of the current was also reversed. This cell likewise failed to develop any activity when set up in the usual

¹ Readings every twenty-four hours.

² Readings every forty-eight hours.

manner. When it was broken a perfectly uniform deposit of the sulphide was found located just within the inner wall. Several subsequent attempts to obtain an active membrane of cadmium sulphide gave the same negative results. This was the only compound investigated which failed completely to show any activity.

CONCLUSIONS.

This investigation has shown :

1. That the electrolytic method is well adapted to the deposition, upon or within porous walls, of precipitates which can be formed from electrolytes in solution.
2. That it affords a ready means of determining which of the precipitates, so deposited, possess a semipermeable character.
3. That the number of compounds possessing a semipermeable character is very large, only one of the ten investigated having failed to show osmotic activity.
4. That there is not immediately, complete diffusion of the water as it enters the cell, but, on the contrary, some of the water rises to the top of the cell and hence the liquid delivered at any time is less concentrated than that of the cell.
5. That of the membranes investigated, the results obtained with zinc and nickel ferrocyanide, and nickel and copper cobalticyanide make it appear very probable that these membranes will be quite as satisfactory as the copper ferrocyanide membrane for measuring high osmotic pressures, when suitable porous vessels are obtained in which to deposit the membranes.
6. All of the membranes prepared in the course of this work proved to be somewhat permeable to sugar, but whether this leakage was the fault of the membranes, or of the very imperfect porous vessels which were used, was not determined. Certain experiments made by others in this laboratory, indicate, however, that the leakage of sugar from any given cell is greatly diminished by a repetition of the membrane-forming process.

BIOGRAPHICAL SKETCH.

The author was born in Hanover, York County, Pennsylvania, on September 10, 1878. His early education was obtained in the public schools of his native town. In 1896, he entered Pennsylvania College, from which he graduated in June, 1900, with the degree of Bachelor of Science. Since the fall of the same year he has been a graduate student in chemistry in the Johns Hopkins University.

